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THE AVERAGE OF AN ANALYTIC FUNCTIONAL[1]

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1. Conceive a particle free to wander along the x-axis. Suppose the probability that it wander a given distance independent

(1) of the position from which it starts to wander,

(2) of the time when it starts to wander,

(3) of the direction in which it wanders.

It may be shown[2] that under these circumstances, the probability that after a time, t, it has wandered from the origin to a position lying between $x=x_0$ and $x=x_1$ is

$$\frac{1}{\sqrt{\pi ct}}\int_{x_0}^{x_1} e^{-\frac{x^2}{ct}}\,dx$$

where t is the time and c is a certain constant which we can reduce to 1 by a proper choice of units. This choice we shall make in what follows. The exponential form of this integral needs no comment, while the mode in which t enters results from the fact that

$$\frac{1}{\sqrt{\pi(t_1+t_2)}}\int_{x_0}^{x_1} e^{-\frac{x^2}{t_1+t_2}}\,dx=\frac{1}{\sqrt{\pi t_1}}\int_{-\infty}^{\infty}\left[\frac{1}{\sqrt{\pi t_2}}\int_{x_0}^{x_1} e^{-\frac{(y-z)^2}{t_2}}\,dy\right]e^{-\frac{z^2}{t_1}}\,dx$$

This identity will be presupposed in all that follows.

Let us now consider a particle wandering from the origin for a given period of time, say from $t=0$ to $t=1$. Its position will then be a function of the time, say $x=f(t)$. There are certain quantities—functionals—which may depend on the whole set of values of f from $t=0$ to $t=1$. If we take a large number of particles (i.e. a large number of values of f) at random, it is natural to suppose that the average value of the functional will often approach a limit, which we may call the average value of the functional over its entire range. What will this average be, and how shall we find it?

If $F\{f\}$ is a functional depending on the values of f for only a finite num-

ber of values of the argument of f—if $F\{f\}$ is a function[3] of $f(t_1)$, $f(t_2)$,..., $f(t_n)$ of the form $\Phi[f(t_1), \ldots, f(t_n)]$—then it is easy enough to give a natural definition of the average of F, which we shall write $A\{F\}$. We can reasonably say

$$A\{F\} = \frac{1}{\sqrt{\pi^n t_1(t_2-t_1)\ldots(t_n-t_{n-1})}} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \Phi(x_1, \ldots, x_n) e^{-\frac{x_1^2}{t_1} - \frac{(x_2-x_1)^2}{t_2-t_1} - \ldots - \frac{(x_n-x_{n-1})^2}{t_n-t_{n-1}}} dx_1 \ldots dx_n.$$

In particular if $F\{f\} = [f(t_1)]^{m_1}[f(t_2)]^{m_2} \ldots [f(t_n)]^{m_n}$, then

$$A\{F\} = \frac{1}{\sqrt{\pi^n t_1(t_2-t_1)\ldots(t_n-t_{n-1})}} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} x_1^{m_1} \ldots x_n^{m_n} e^{-\frac{x_1^2}{t_1} - \ldots - \frac{(x_n-x_{n-1})^2}{t_n-t_{n-1}}} dx_1 \ldots dx_n$$

$$= \frac{1}{\sqrt{\pi^n t_1(t_2-t_1)\ldots(t_n-t_{n-1})}} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} y_1^{m_1}(y_2+y_1)^{m_2}\ldots(y_n+y_{n-1}+\ldots + y_1)^{m_n} e^{-\frac{y_1^2}{t_1} - \ldots - \frac{y_n^2}{t_n-t_{n-1}}} dy_1 \ldots dy_n$$

$$= \frac{1}{\sqrt{\pi^n}} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} (t_1^{1/2}z_1)^{m_1}\left[(t_2-t_1)^{1/2}z_2 + t_1^{1/2}z_1\right]^{m_2} \ldots \left[(t_n-t_{n-1})^{1/2}z_n + \ldots + t_1^{1/2}z_1\right]^{m_n} e^{-z_1^2 - \ldots - z_n^2} dz_1 \ldots dz_n.$$

This latter integral is in the form

$$\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} P(z_1, \ldots, z_n) e^{-z_1^2 - \ldots - z_n^2} dz_1, \ldots dz_n$$

where P is a polynomial, and can be evaluated by means of the well known formulae:

$$\int_{-\infty}^{\infty} e^{-y^2} y^{2n+1} dy = 0,$$

$$\int_{-\infty}^{\infty} e^{-y^2} y^{2n} dy = \sqrt{\pi}\, \frac{1.3.5\ldots(2n-1)}{2^n}.$$

We can thus easily evaluate $A\{F\}$ as a polynomial in $t_1, t_2, \ldots, t_n$, which we shall call $P_{m_1, \ldots, m_n}(t_1, \ldots, t_n)$. It is easy to show that if Σm_k is odd,

$$P_{m_1, \ldots, m_n}(t_1, \ldots, t_n) = 0.$$

To return to the more general functional: there is a large class of so-called analytic functionals,[4] which may be expanded in the form of series such as

$$F\{f\} = a_0 + \int_0^1 f(x)\varphi_1(x)dx + \int_0^1\int_0^1 f(x)\,f(y)\varphi_2(x,y)dxdy + \ldots$$
$$+ \int_0^1 \ldots \int_0^1 f(x_1)\ldots f(x_n)\varphi_n(x_1, \ldots, x_n)\,dx_1 \ldots dx_n + \ldots$$

and an even wider class of what may be called Stieltjes analyt ic functionals, in which the general term

$$\int_0^1 \ldots \int_0^1 f(x_1)\ldots f(x_n)\varphi_n(x_1, \ldots, x_n)dx_1, \ldots dx_n$$

is replaced by the Stieltjes integral[5]

$$\int_0^1 \ldots \int_0^1 f(x_1)\ldots f(x_n)d\psi_n(x_1, \ldots, x_n).$$

In what follows, we shall confine our discussion to Stieltjes analytic functionals, which we shall call simply analytic. The problem with which we are now concerned is the definition of the average of an analytic functional. Now, the first property which any average ought to fulfil is that the average of the sum of two functionals should equal the sum of their averages. We should expect, therefore, that:

(*a*) Over a wide range of cases, the average of a series should equal the series of the averages of the terms;

(*b*) The average of a Stieltjes integral, single or multiple, of a given functional with respect to such parameters as it may contain, should be equal to the integral of the average;

(*c*) A constant multiplied by the average of a functional should equal the average of a constant times the functional.

In accordance with this, we get the following natural definition of the average of the analytic functional F.

$$A\{F\} = A\{a_0 + \int_0^1 f(x)d\psi_1(x) + \int_0^1\int_0^1 f(x)\,f(y)d\psi_2(x,y) + \ldots\}$$
$$= a_0 + A\left\{\int_0^1 f(x)d\psi_1(x)\right\} + A\left\{\int_0^1\int_0^1 f(x)\,f(y)d\psi_2(x,y)\right\} + \ldots$$
$$= a_0 + \int_0^1 A\{f(x)\}d\psi_1(x) + \int_0^1\int_0^1 A\{f(x)f(y)\}d\psi_2(x,y) + \ldots$$

We have already seen how to determine $A\{f(x_1)\ldots f(x_n)\}$ as a polynomial in the x_k's. Hence whenever the above series converges, we have now a way of obtaining a perfectly definite value for $A\{F\}$. It may be noted that every term in the above expression in which the sign of integration is repeated an odd number of times is identically zero.

If $A\{F\}$ is to behave as we should expect it to behave, there are certain properties which it must fulfil, at least over a large and important class of cases. Among these are the following:

(1) $A\{F_1\} + A\{F_2\} = A\{F_1 + F_2\}$

(2) $cA\{F_1\} = A\{cF_1\}$

(3) $\sum_1^\infty A\{F_n\} = A\left\{\sum_1^\infty F_n\right\}$

(4) If F_x is a functional depending on the parameter x, and $u(x)$ is a function of limited total variation, then

$$\int_a^b A\{F_x\}du = A\left\{\int_a^b F_x du\right\}$$

(5) Suppose $F_{t_1,\ldots,t_n}(x_1, \ldots, x_n)$ be defined as $F\left\{f^{x_1,\ldots,x_n}_{t_1,\ldots,t_n}(t)\right\}$, where $f^{x_1,\ldots,x_n}_{t_1,\ldots,t_n}(t)$ assumes the value

$$x_k + \frac{(t - t_k)(x_{k+1} - x_k)}{t_{k+1} - t_k}$$

for $t_k \leq t \leq t_{k-1}$. Then

$$A\{F\} = \lim \pi^{-\frac{n}{2}} \prod_1^n (t_k - t_{k-1})^{-1/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} F_{t_1,\ldots,t_n}(x_1, \ldots, x_n)$$
$$e^{-\frac{x_1^2}{t_1} - \sum_2^n \frac{(x_k - x_{k-1})^2}{(t_k - t_{k-1})}} dx_1 \ldots dx_n,$$

where the limit is taken as the t_k's increase in number in such a manner to divide the interval from 0 to 1 more and more finely.

2. The next task before us is to investigate hypotheses which are sufficient to guarantee the validity of propositions (1)–(5). Propositions (1) and (2) require indeed very little discussion, for they are always satisfied when the series for F_1, F_2, $A\{F_1\}$ and $A\{F_2\}$ converge. In (3), let $F_1, \ldots, F_n, \ldots$, and the series ΣF_n all possess averages, and let

$$\sum_1^\infty F_n = \sum_1^m F_n + R_m$$

where $A\{R_m\}$ vanishes as m increases without limit. Then

$$A\left\{\sum_1^\infty F_n\right\} = \sum_1^m A\{F_n\} + A\{R_m\}.$$

Therefore

$$\lim_{m=\infty} \left| A\left\{\sum_1^\infty F_n\right\} - \sum_1^m A\left\{F_n\right\} \right| = 0$$

and (3) is proved. If ΣF_n converges and $\lim A\{R_m\} = 0$, we shall say ΣF_n converges *smoothly*.

Proposition (4) reduces to the ordinary inversion of a multiple Stieltjes integral when $F_x\{f\}$ is of the form

$$\int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n) d\psi_n(x_1, \ldots, x_n, x)$$

and ψ_n is a function of limited variation in $x_1, \ldots, x_n$. What we wish to prove is that

$$\int_a^b \left\{ \int_0^1 \cdots \int_0^1 A\{f(x_1) \ldots f(x_n)\} d\psi_n(x_1, \ldots, x_n) \right\} du$$
$$= A\left\{ \int_a^b \left\{ \int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n)\, d\psi_n\,(x_1, \ldots, x_n) \right\} du \right\}$$

Now

$$\int_a^b \left\{ \int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n)\, d\psi_n\,(x_1, \ldots, x_n) \right\} du =$$
$$\int_a^b \left[\lim \sum_{\alpha, \ldots, \vartheta} f(\xi_{1\alpha}) \ldots f\,(\xi_{n\vartheta})\, \Delta \begin{matrix} x_1, \alpha+1 \ldots x_n, \vartheta+1 \\ x_{1\alpha} \ldots x_{n\vartheta} \end{matrix} \psi_n(x_1, \ldots, x_n, x) \right] du.$$

If in this latter expression the total variation of ψ_n is less than a quantity independent of x, we can permute the $\int_a^b$ and the *lim*, and get

$$\lim \sum_{\alpha, \ldots, \vartheta} f(\xi_{1\alpha}) \ldots f(\xi_{n\vartheta})\, \Delta \begin{matrix} x_1, \alpha+1 \ldots x_n, \vartheta+1 \\ x_{1\alpha} \ldots x_{n\vartheta} \end{matrix} \int_a^b \psi_n\,(x_1, \ldots, x_n, x)\, du,$$

which we may write

$$\int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n) d\left[\int_a^b \psi_n(x_1, \ldots, x_n, x)\, du \right].$$

In this we suppose f uniformly continuous. It is easy to show that on our assumptions $\int_a^b \psi_n(x_1, \ldots, x_n, x) du$ is of limited variation. Consequently we obtain

$$A\left\{ \int_a^b \left\{ \int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n) d\psi_n(x_1, \ldots, x_n, x) \right\} du \right\}$$
$$= A\left\{ \int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n) d\left[\int_a^b \psi_n(x_1, \ldots, x_n, x) du \right] \right\}$$
$$= \int_0^1 \cdots \int_0^1 A\{f(x_1) \ldots f(x_n)\} d\left[\int_a^b \psi_n(x_1, \ldots, x_n, x)\, du \right].$$

A further transformation just like the preceding turns this into

$$\int_a^b \left\{ \int_0^1 \cdots \int_0^1 A\{f(x_1) \ldots f(x_n)\} d\psi_n\,(x_1, \ldots, x_n, x) \right\} du$$

so that we have now a sufficient condition for the validity of our theorem. The extension to non-homogeneous terminating analytic functionals is obvious. The extension to non-terminating analytic functionals may be deduced with the help of (3) and a well-known theorem on the integration of uniformly convergent series, and reads as follows: *let* F_x, *be an analytic functional of the form*

$$a_0 + \sum_1^\infty \int_0^1 \cdots \int_0^1 f(x_1) \ldots f(x_n)\, d\psi_n(x_1, \ldots, x_n, x)$$

where the total variation of each ψ_n is less than some quantity independent of x, and let each ψ_n be uniformly continuous in x over the interval (a, b). Let $u(x)$ be a function of limited total variation in x over the same interval. Let $A\{\int_a^b F_x du\}$ exist, and let

$$\lim_{m=\infty} \sum_{n=m}^{\infty} \int_0^1 \cdots \int_0^1 A\{f(x_1) \cdots f(x_n)\}\, d\psi_n(x_1, \ldots, x_n, x) = 0$$

uniformly in x. Then

$$\int_a^b A\{F_x\} du = A\left\{\int_a^b F_x\, du\right\}.$$

As to (5), let us begin as above with a functional of the form

$$\Phi\{f\} = \int_0^1 \cdots \int_0^1 f(x_1) \cdots f(x_n)\, d\psi_n(x_1, \ldots, x_n).$$

Consider

$$I = \int_0^1 \cdots \int_0^1 A\{f(x_1) \cdots f(x_n)\}\, d\psi_n(x_1, \ldots, x_n),$$

where A is taken in the original sense as an n-fold integral. By definition

$$I = \lim \sum_{\alpha, \ldots, \vartheta} A\{f(\xi_{1\alpha}) \cdots f(\xi_{n\vartheta})\}\, \Delta^{x_{1,\alpha+1} \cdots x_{n,\vartheta+1}}_{x_{1\alpha} \cdots x_{n\vartheta}} \psi_n(x_1, \ldots, x_n),$$

where $x_{k0} = 0, x_{k1}, \ldots, x_{k\mu} = 1$ is an increasing sequence of numbers, ξ_{kK} lies between x_{kK} and $x_{k,K+1}$ and *lim* is taken as $max(x_{k,K+1} - x_{kK})$ approaches 0. Let V be the total variation of ψ_n as its arguments range from 0 to 1, and let M stand for $max(x_{k,K+1} - x_{kK})$. Let Q stand for the least upper bound of the variation of $A\{f(x_1) \cdots f(x_n)\}$ as the point $(x_1, \ldots, x_n)$ wanders over an interval $\binom{x_{1,\alpha+1} \ldots x_{n\vartheta+1}}{x_{1\alpha} \ldots x_{n\vartheta}}$. Then

$$(6) \quad \left| I - A\left\{ \sum_{\alpha, \ldots, \vartheta} f(\xi_{1\alpha}) \cdots f(\xi_{n\vartheta}) \Delta^{x_{1,\alpha+1} \ldots x_{n,\vartheta+1}}_{x_{1\alpha} \ldots x_{n\vartheta}} \psi_n(x_1, \ldots, x_n) \right\} \right| \leq VQ.$$

Now, let $f_m(x)$ be that function whose graph is the broken line with corners at $(x_{(K)}, f(x_{(K)}))$, where $0 \leq K \leq \mu, x_{(0)} = 0, x_{(\mu)} = 1$. Then if x lies between $x_{(K)}$ and $x_{(K+1)}$, $f_m(x)$ is of the form $af_m(x_{(K)}) + bf_m(x_{(K)}) \div a + b$. It follows that if $(\xi_{1\alpha}, \ldots, \xi_{n\vartheta})$ lies in the interval $\binom{x_{(\alpha+1)} \ldots x_{(\vartheta+1)}}{x_{(\alpha)} \ldots x_{(\vartheta)}}$, $A\{f_m(\xi_{1\alpha}) \cdots f_m(\xi_{n\vartheta})\}$ is of the form

$$\frac{a_1 C_1 + a_2 C_2 + \ldots + a_\rho C_\rho}{a_1 + a_2 + \ldots + a_\rho}$$

where each C_k is the value of some $A\{f(\xi_{1\alpha}) \cdots f(\xi_{\eta\vartheta})\}$ such that $(\xi_{1\alpha}, \ldots, \xi_{\eta\vartheta})$ is a corner of the hyperparallelopiped $\binom{x_{(\alpha+1)} \ldots x_{(\vartheta+1)}}{x_{(\alpha)} \ldots x_{(\vartheta)}}$. It readily results from considerations of continuity that $A\{f_m(\xi_1) \cdots f_m(\xi_\mu)\}$ is of the form $A\{f(\eta_{1\alpha}) \cdots f(\eta_{n\vartheta})\}$, where $(\eta_{1\alpha}, \ldots, \eta_{n\vartheta})$ also lies in the interval $\binom{x_{(\alpha+1)} \ldots x_{(\vartheta+1)}}{x_{(\alpha)} \ldots x_{(\vartheta)}}$.

Making use of this fact, and of the fact that

$$\frac{1}{\sqrt{\pi^n t_1(t_2-t_1)\dots(t_n-t_{n-1})}}\int_{-\infty}^{\infty}\dots\int_{-\infty}^{\infty}\Phi(x_1,\dots,x_n)\,e^{-\frac{x_1^2}{t_1}-\dots-\frac{(x_n-x_{n-1})^2}{t_n-t_{n-1}}}\,dx_1\dots dx_n$$

is an increasing functional of $\Phi(x_1,\dots,x_n)$, we can draw the conclusion that

$$A\{\Phi\{f_m\}\}=A\left\{\int_0^1\dots\int_0^1 f_m(x_1)\dots f_m(x_n)\,d\psi_n(x_1,\dots,x_n)\right\}$$

if it exists, lies between the uppermost and lowermost values of

$$\sum_{\alpha,\dots,\vartheta}A\{f_m(\xi_{1\alpha})\dots f_m(\xi_{n\vartheta})\}\Delta_{x(\alpha)\dots x(\vartheta)}^{x(\alpha+1)\dots x(\vartheta+1)}\psi_n(x_1,\dots,x_n)$$

and hence of

$$\sum_{\alpha,\dots,\vartheta}A\{f(\eta_{1\alpha})\dots f(\eta_{n\vartheta})\}\Delta_{x(\alpha)\dots x(\vartheta)}^{x(\alpha+1)\dots x(\vartheta+1)}\psi_n(x_1,\dots,x_n)$$

From this and (6) we can deduce

$$|\mathrm{I}-A\{\Phi\{f_m\}\}|\leq 2VQ \tag{7}$$

where Q is taken for $x_{hK}=x(K)$.

This proves our theorem for homogeneous analytic functionals. In precise terms, then, our general theorem will read: *let*

$$F\{f\}=a_0+\sum_1^\infty\int_0^1\dots\int_0^1 f(x_1)\dots f(x_n)\,d\psi_n(x_1,\dots,x_n)=a_0+\sum_1^\infty F_n\{f\}$$

be an analytic functional. Let V_n stand for the total variation of F_n as its arguments range from 0 to 1: Let $(x_{(0)},\dots,x_{(\mu)})$ be a set of numbers in ascending order from 0 to 1, inclusive. Let M stand for max $(x_{(K+1)}-x_{(K)})$ and Q_n for the upper bound of the variation of $A\{f(x_1)\dots f(x_n)\}$ as the point $(x_1,\dots,x_n)$ wanders over the interval $\binom{x(\alpha+1)\dots x(\vartheta+1)}{x(\alpha)\dots x(\vartheta)}$. Let $f_\mu(x)$ be the function whose graph is the broken line with corners at $(0,0)$ and $(x_{(K)},f(x_{(K)}))$. Then if

(a) $$\lim_{M=0}\sum_1^\infty V_kQ_k=0,$$

(b) $A\{F_n\{f_\mu\}\}$ *exists for every μ and n according to the definition of A as a multiple integral:*

(c) *the series for F converges smoothly;*

(d) $\lim_{n=\infty}A\left\{\sum_n^\infty F_m\{f_\mu\}\right\}$ *exists for every μ, when A is taken as a multiple integral; it follows that*

$$A\{F\}=\lim_{M=0}A\{F\{f_m\}\},$$

where the first A is defined in the sense of the average of an analytic functional, and the second as a multiple integral. A precisely analogous theorem holds when $f_m(x)$ instead of a broken straight line is any broken line with corners at $(0, 0)$ and at $(x_{(K)}, f(x_{(K)}))$, and consists of monotone arcs between these points. This last theorem makes our average of a functional the limit of the average of a function of a discrete set of variables, and justifies our use of the term average.

[1] The problem of the mean of a functional has been attached by Gâteaux (*Bull. Soc. Math. de France*, 1919, pp. 47–70). The idea of using the analytic functional as a basis is there found. The actual definition, however, is essentially different, and does not lend itself readily to the treatment of the Brownian Movement, for which the present method is especially adapted.

[2] Einstein, *Leipzig, Annalen Physik*, 17, 905.

[3] We here take $l_1, <l_2< \ldots < l_n$.

[4] Cf. V. Volterra, *Fonctions des Lignes*.

[5] Cf. P. J. Daniell, *Annals of Mathematics*, Sept., 1919, p. 30.

ON THE CALCULATION OF THE X-RAY ABSORPTION FREQUENCIES OF THE CHEMICAL ELEMENTS

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The K critical absorption frequency of a chemical element is the highest frequency of vibration known to be characteristic of that element. In our laboratory we have measured the K critical absorption frequencies of most of the chemical elements by the ionization method. This data, together with measurements made elsewhere by the photographic method, may be found in Table 2 of a report by the author on Data Relating to X-Ray Spectra, which has been published by the National Research Council.

At a symposium on Ultra-Violet Light and X-Rays, held at the meeting of the American Association for the Advancement of Science at St. Louis in December 1919,[1] I presented a set of computations of the K critical absorption frequencies based on the Rutherford-Bohr theory of atomic structure and the mechanism of radiation. The computed values equalled the observed values to within one or two per cent. In these computations the electrons were supposed to revolve in orbits which lay in planes passing through the nucleus of the atom.

Later I presented[2] to the National Academy of Sciences and to the American Physical Society computations of these K critical absorption frequencies, calculated on the assumption that the orbits did not all lie in planes through the nucleus. I assumed that the orbits were cir-

cular, that they occurred in pairs and that the two orbits in a pair lay opposite to each other in parallel planes equi-distant from the nucleus, as represented in the figure. This gives a volume distribution of electrons. The mutual repulsion of the electrons for each other keep the orbits apart. It is necessary, however, to suppose that the electrons in the two orbits of a pair revolve in opposite directions. Otherwise they would be pulled together to form a single orbit in a plane through the nucleus (at least for elements of high atomic numbers). The revolution in opposite directions has the advantage, among others, of reducing the magnetic field due to the electrons for points at a distance from the atom to a very small value.

The theory contains three fundamental laws. The acceleration law, the angular momentum law and the frequency law. The acceleration law states that the centripetal acceleration of each electron revolving in its orbit equals the centripetal force acting on it, due to the attraction and repulsion of all the electrical charges in the atom acting according to Coulomb's inverse square law. The angular momentum law states that the angular momentum of each electron equals a whole number (called the quantum number), τ, multiplied by Planck's action constant, h, and divided by 2π. According to the frequency law, the product of h into the frequency of vibration, ν, of the radiation emitted during a shift of the electrons from one position of dynamic equilibrium to another equals the difference in the amounts of energy in the atom before and after the shift.

The first two laws cannot be true at every instant of time. One or both of them must represent average values. In the modern development of the theory a definite integral of certain generalized coördinates is equated to a multiple of h.

The theory does not determine the numbers of electrons in the various orbits. In making calculations, however, we must know how the electrons are distributed. Several authors have calculated X-ray frequencies by choosing distributions of electrons in the orbits that best fit the X-ray data themselves. I have taken a distribution suggested by the intervals between the inert gases in the sequence of chemical elements. It has long been supposed that these intervals correspond to groups of electrons in the atom that are completely filled up. From this point of view we get as the numbers of electrons in the various groups the following: the inner orbit contains two electrons. The next group consists of a pair of parallel orbits containing in all eight electrons, four in each orbit. The third group contains eight electrons, four in each of the two parallel orbits. The next group contains eighteen electrons in all, nine in each of the two parallel orbits. The fifth group also contains eighteen, nine in each orbit. The outside pair of parallel orbits contains thirty-two

electrons, sixteen in each orbit. Of course, for atoms containing less than ninety-two electrons the outer groups are incomplete, or missing altogether.

To each pair of orbits belongs a certain quantum number, τ. For the inner orbit $\tau = 1$, for the second group $\tau = 2$, for the third group $\tau = 2$, for the fourth and fifth $\tau = 3$, and for the sixth group $\tau = 4$. According to this distribution the number of electrons in an orbit (except the innermost) equals the square of the orbit's quantum number.

The fundamental laws of the theory may be expressed by the following equations:

Acceleration Law.....	$mv^2/a =$ Centripetal Force	(1)
Angular Momentum Law.....	$mva = h/2\pi$	(2)
Frequency Law.....	$h\nu = W_1 - W_2$	(3)
Distribution Law.....	$n = \tau^2$	(4)

where m is the mass of an electron, v, its velocity, a, the radius of its orbit, and W_1 and W_2 are the total amounts of energy possessed by the atom in the two states of dynamic equilibrium.

In computing vibration frequencies we first calculate the velocity of each electron from equations 1 and 2, and then find the total energy of all the electrons, including both the potential and kinetic energies. Taking into account the change of mass of an electron with its velocity, the total energy may be represented by

$$W = \Sigma\, m_o c^2(\sqrt{1-\beta^2} - 1),$$

where $\beta = v/c$, c being the velocity of light. If the velocity of the electron is small, as compared with the velocity of light, this expression reduces to

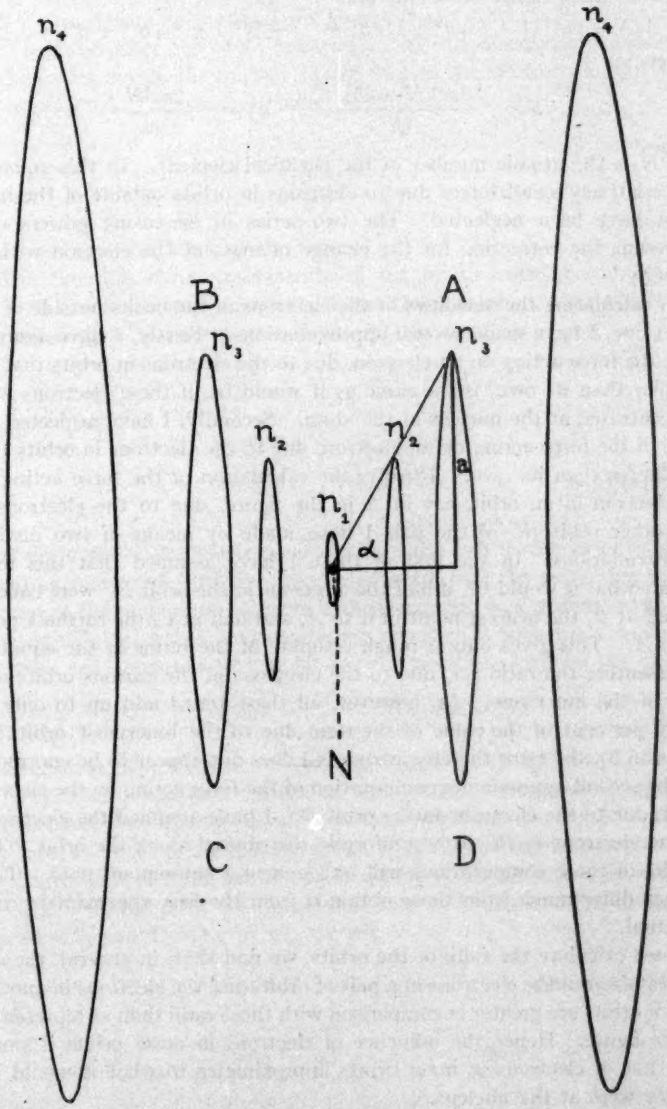
$$W = -\Sigma^1/_2\, m_o v^2.$$

To compute the K critical absorption frequency (according to equation 3) we must calculate the value of W for the atom, when one electron is missing from the inner orbit, and subtract from it the value of W, when this electron is in its proper place. The difference between these two terms equals h multiplied by the critical absorption frequency, ν.

Each of the terms in the expressions obtained for W contains the quantity

$$\nu_o = \frac{2\pi^2 e^4 m_o}{h^3} \qquad (5)$$

as a factor. This is the Rydberg fundamental constant. It simplifies the equations to calculate the ratio of the absorption frequency to this fundamental constant, i.e., ν/ν_o.


n_4
n_4
B
A
n_3
n_3
n_2
n_2
n_1
a
α
N
C
D

The terms in the expression for the frequency ratio ν/ν_0 due to the electrons in the inner orbit only are

$$2(N-.25)^2(1+{}^1/_4\beta^2+{}^1/_8\beta^4+..)-N^2(1+{}^1/_4\beta'^2+\beta'^4+..), \quad (6)$$

where

$$\beta=\frac{2\pi e^2(N-.25)}{ch} \qquad \beta'=\frac{2\pi e^2N}{ch}$$

and N is the atomic number of the chemical element. In this equation the relatively small forces due to electrons in orbits outside of the inner orbit have been neglected. The two series in increasing powers of β represent the correction for the change of mass of the electron with its velocity.

In calculating the velocities of the electrons in the orbits outside of the inner one, I have made several approximations. Firstly, I have assumed that the force acting on an electron, due to the electrons in orbits that are smaller than its own, is the same as it would be, if these electrons were concentrated at the nucleus of the atom. Secondly, I have neglected the part of the force acting on an electron, due to the electrons in orbits that are larger than its own. Thirdly, the calculation of the force acting on an electron in an orbit, say at A in the figure, due to the electrons in the other orbit BC of the pair I have made by means of two distinct approximations. In the first of these I have assumed that this force equals what it would be, if half the electrons in the orbit BC were concentrated at B, the nearest point in it to A, and half at C, the furthest point from A. This gives only a rough estimate of the terms in the equation representing the ratio ν/ν_0 due to the electrons in the various orbits outside of the inner one. As, however, all these terms add up to only 15 or 20 per cent of the value of the term due to the innermost orbit (expression 6), the error thereby introduced does not appear to be enormous. In the second approximate computation of the force acting on the electron at A, due to the electrons in the orbit BC, I have assumed the electricity of the electrons in BC to be uniformly distributed along the orbit. The results of these computations will be given in a subsequent note. They do not differ much from those obtained from the first approximate computation.

If we calculate the radii of the orbits, we find that, in general, the distances between the electrons in a pair of orbits and the electrons in another pair of orbits are greater in comparison with those radii than as represented in the figure. Hence the influence of electrons in outer orbits is small, and that of electrons in inner orbits approximates to what it would be, if they were at the nucleus.

To calculate the velocity of an electron, say at A, we first calculate the angle α in the figure as follows: Let N' be the total number of electron

charges inside the orbits $A\ B\ C\ D$. N' then equals the atomic number of the chemical element N less the number of electrons inside the orbits $A\ B\ C\ D$. Assuming that half the charge in the orbit BC is concentrated at B and the other half at C, equating to zero the horizontal components of the forces due to the nuclear charge and to the electrons in and inside of the orbits $A\ B\ C\ D$ and reducing we get the equation

$$\cos^3\alpha = \frac{1}{\frac{8}{n}N' - 1}, \tag{7}$$

which gives us the value of the angle α.

Equating the radial components of the forces acting on an electron at A to the centripetal acceleration, multiplying by a^2, and substituting the value of N' from equation 7, we get the equation

$$mv^2a = e^2\left(\frac{n}{8}\tan^3\alpha - s_n\right) \tag{8}$$

where

$$s_n = {}^1/_4 \sum_{s=1}^{s=n-1} \operatorname{cosec}\frac{s}{n} \tag{9}$$

The velocities of the electrons other than the two in the inner orbit are small as compared with the velocity of light, and the correction for the change of the mass of an electron with its velocity is, therefore, negligible. Neglecting this change and combining equation 8 with the angular momentum law (equation 2) we get for the kinetic energy of the electron

$${}^1/_2 mv^2 = \frac{2\pi^2e^4m}{h^2\tau^2}\left(\frac{n}{8}\tan^3\alpha - s_n\right)^2 \tag{10}$$

where the angle α is given by equation 7, and s_n, by equation 9.

In systems of the kind considered, the potential energy of the electrons equals twice their kinetic energy with the negative sign before it.[3] Hence, the total energy, kinetic plus potential, is minus the kinetic energy. Substituting the expression for the total energy of all the electrons with one electron removed from the inner orbit, and with this electron in place in equation 3, and dividing by $h\nu_o$, we get

$$\frac{\nu}{\nu_o} = 2(-N.25)^2(1+{}^1/_4\beta^2+{}^1/_8\beta^4+\ldots) - N^2(1+{}^1/_4\beta'^2+{}^1/_8\beta'^4+\ldots)$$

$$+ \Sigma\frac{2n}{\tau^2}\left(\frac{n}{8}\tan^3\alpha - s_n\right)^2 - {}_n\Sigma\frac{2n}{\tau^2}\left(\frac{n}{8}\tan^3\alpha' - s_n\right)^2 \tag{11}$$

as the expression for the critical absorption frequency of the chemical element divided by the Rydberg constant.

Table 1 contains the calculated and the observed values of the ratio ν/ν_0'. The observed values I have taken from table 2 of the report on Data Relating to X-Ray Spectra which I compiled for the National Research Council. Column 4 in the table contains the observed values, and column 3 the values calculated according to the following scheme:

$$n_1 = 2, \quad n_2 = 4, \quad n_3 = 4, \quad n_4 = 9, \quad n_5 = 9, \quad n_6 = 16,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 2, \quad \tau_4 = 3, \quad \tau_5 = 3, \quad \tau_6 = 4.$$

TABLE 1

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT ν/ν_0		
		Calculated	Observed	Calculated
Magnesium	12	103.2	95.8	92.5
Sulphur	16	187.4	181.8	173.3
Calcium	20	297.7	297.5	279.7
Iron	26	521.0	523.8	494.9
Selenium	34	923.3	930.8	888.7
Molybdenum	42	1454.0	1474.0	1411.0
Tin	50	2125.0	2148.0	2063.0
Cerium	58	2918.0	2970.0	2860.0
Dysprosium	66	3896.0	3948.0	3820.0
Tungsten	74	5043.0	5118.0	4954.0
Lead	82	6404.0	6463.0	6270.0
Uranium	92	8468.0	8477.0	8345.0

It appears that, except in the case of the elements magnesium and sulphur, the calculated values in column three do not differ from the observed values by as much as two per cent. Considering the fact that the equations contain no undetermined constants after the distribution law has been fixed and considering the fact that various influences have been neglected, such as magnetic forces, forces due to electrons in outer orbits, the possible influence of electrons which may be forming bonds with other atoms, etc., the close agreement between the calculated and observed values appears extraordinary.

I have also calculated the absorption frequencies, assuming a distribution according to the scheme

$$n_1 = 2, \quad n_2 = 8, \quad n_3 = 18, \quad n_4 = 32,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 3, \quad \tau_4 = 4.$$

The calculated values based on this scheme do not differ very much from those contained in column 3 of the table. It appears, therefore, that the calculation of the K critical absorption frequencies does not furnish a very sensitive method of determining exactly what the distribution of electrons is. It is important to note, however, that two electrons have a quantum number of one, sixteen electrons have a quantum

number of two, thirty-six electrons have a quantum number of three, etc.

On examining the data closely we find a systematic deviation of the calculated from the observed values. This deviation becomes most marked in the elements of low atomic number. It lies in the same direction as the well-known difference between the observed and calculated ionizing potentials of helium.

In order to see whether a better representation of facts can be obtained by supposing that the two inner electrons revolve in opposite directions in separate orbits, I have made the calculations on that basis. The only difference in formula 11 occurs in the terms representing the innermost orbit. The first two terms of equation 11 must be replaced by the single term.

$$(N-1)^2 (1 + {}^1/_4 \beta'^2 + {}^1/_8 \beta'^4 + \ldots) \qquad (12)$$

Column 5 of the table contains the results of the computations. It appears from the data of column 5 that the observed and calculated values differ from each other by amounts up to $4^1/_2\%$. A systematic variation exists which increases as the atomic weight decreases, and which lies in the opposite direction to that represented by the data of column 3.

[1] *Science*, May 21, 1920.

[2] Fall Meeting of the National Academy of Sciences, 1920; *Physic. Rev.*, March, 1921, p. 431.

[3] This can be proved easily for the particular case in question. For a proof of the theorem in a more general form see A. Sommerfeld, *Atombau und Spektrallinien*, Appendix 5.

ON THE CALCULATION OF THE X-RAY ABSORPTION FREQUENCIES OF THE CHEMICAL ELEMENTS (SECOND NOTE)

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Communicated July 25, 1921

In a note presented to the National Academy of Sciences[1] I have given some computations of the K critical absorption frequencies of the chemical elements based on the Rutherford-Bohr theory of the structure of atoms and the mechanism of radiation. In these computations I have assumed that the electrons were distributed in circular orbits, which did not lie in planes passing through the nucleus of the atom.

In order to estimate roughly the forces exerted on an electron in one orbit (A in the figure of the previous note) due to the electrons in the parallel orbit, I assumed that they were the same as if the charges of the electrons in the orbit BC were concentrated, half at the nearest point

in the orbit to A, and half at the furthest point in the orbit from A. In the computations presented in this note I assume that the forces are the same as if the electricity of the electrons in the orbit BC were uniformly distributed along the orbit. As in the previous note, I neglect the forces acting on an electron at A, due to the electrons in the orbits that are larger than the orbits $A\ B\ C\ D$, and assume that the forces due to the electrons in the orbits smaller than $A\ B\ C\ D$ are the same as if these electrons were concentrated at the nucleus of the atom.

The terms in the expression for the ratio of the critical absorption frequency to the Rydberg constant, ν/ν_0, due to the two innermost electrons, are the same as in the previous case (expressions 6 and 12 of the previous note). To get the correction term due to the electrons in the orbits outside of the inner orbit we proceed as follows: Equating to zero the horizontal components of the forces acting on an electron at A due to the nucleus and to the electrons inside and in the orbits $A\ B\ C\ D$, we get the equation

$$N' cos^3\alpha = \frac{n}{2\pi}\int_0^{\frac{\pi}{2}} \frac{d\theta}{(1 + tan^2\alpha\ sin^2\theta)^{3/2}}$$

where θ is half the angle made by the radius of the orbit BC drawn to any point in the orbit with the vertical.

Similarly, equating the centripetal acceleration of the electron at A to the centripetal force acting on it, due to the nucleus, to the electrons inside the orbits $A\ B\ C\ D$ and to the electricity of the orbit BC, and reducing, we get the equation

$$mv^2a = N' sin^3\alpha - nB - s_n, \tag{14}$$

$$\text{where } B = \frac{tan^3\alpha}{2\pi}\int_0^{\frac{\pi}{2}} \frac{sin^2\theta\, d\theta}{(1 + tan^2\alpha\ sin^2\theta)^{3/2}} \tag{15}$$

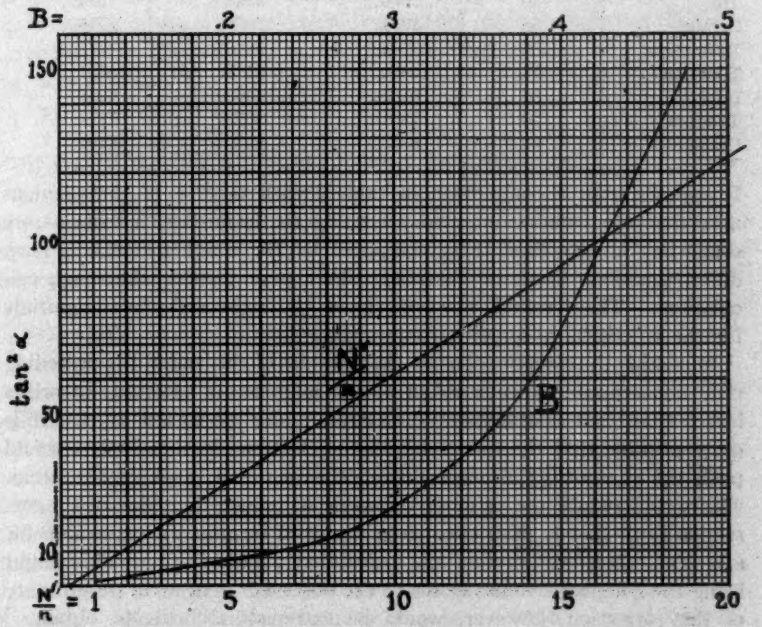
and where s_n is given by equation 9 of the previous note.

Combining equation 14 with equation 2 of the previous note, representing the angular momentum law, we get an expression similar to equation 10 for the kinetic energy of the electron at A. Taking the sum of these expressions for all the electrons with one of the electrons of the inner orbit removed and with it in place, and substituting in formula 3, representing the frequency law, we get the equation for ν/ν_0

$$\frac{\nu}{\nu_0} = 2(N-.25)^2(1 + {}^1/_2\beta^2 + {}^1/_8\beta^4 + ..) - N^2(1 + {}^1/_4\beta'^2 + {}^1/_8\beta^{14} + ..)$$
$$+ \sum \frac{2n}{\tau^2}\,[N' sin^3\alpha - nB - s_n]^2$$

$$-\sum \frac{2n}{\tau^2}\left[(N'+1)\sin^2\alpha' - nB' - s_n\right]^2 \qquad (16)$$

where α is related to N' and n according to equation 13, and B is given by equation 15, and where α' and B' are obtained from the same equations by substituting $N'+1$ for N'. For purposes of computation I have performed the indicated integrations by graphical methods and plotted curves representing N'/n and B as functions of $\tan^2\alpha$. The curves appear in the figure. The relation of N'/n to $\tan^2\alpha$ is almost linear. By using these curves to determine the values of α and α' corresponding to various values of N'/n and $(N'+1)/n$, respectively, and then the values of B



and B' corresponding to those values of α and α', the data of table 2 has been computed. Columns 3 and 5 in table 2 contain values computed on a distribution of electrons represented by the scheme

$$\begin{array}{llllll} n_1 = 1, & n_2 = 4, & n_3 = 4, & n_4 = 9, & n_5 = 9, & n_6 = 16, \\ \tau_1 = 1, & \tau_2 = 2, & \tau_3 = 2, & \tau_4 = 3, & \tau_5 = 3, & \tau_6 = 4. \end{array}$$

The data in column 5 has been computed under the assumption that the two electrons nearest the nucleus revolve in opposite directions in separate orbits, one outside the other; whereas for the data of column 3 they are supposed to revolve in the same orbit.

TABLE 2

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT, ν/ν_0		
		Calculated	Observed	Calculated
Magnesium	12	103.3	95.8	92.6
Sulphur	16	181.1	181.8	167.0
Calcium	20	290.0	297.5	272.0
Iron	26	510.1	523.8	484.0
Selenium	34	918.4	930.8	873.8
Molybdenum	42	1431.	1474.	1388.
Tin	50	2056.	2148.	1994.
Cerium	58	2854.	2970.	2796.
Dysprosium	66	3853.	3948.	3777.
Tungsten	74	4990.	5118.	4901.
Lead	82	6362.	6463.	6228.
Thorium	90	7891.	8075.	7774.
Uranium	92	8313.	8477.	8190.

It appears from a comparison of table 2 with table 1 of the previous note that the values computed according to the integral equations are somewhat smaller than those computed by the rough formulas. They differ, therefore, from the observed values more than do the rough calculations. The formula, however, gives the right order of magnitude for the K critical absorption frequencies.

In making the computations by the formulas of this and of the preceding note no account has been taken of the influence of electrons in orbits larger than that containing the electron under discussion at A. It is quite possible that the forces due to the electrons in these orbits would push the electron at A further from the meridian plane of the atom. This would reduce the value of the angle α, reduce the value of the correction term that is subtracted from the main term in the expression for ν/ν_0, and therefore increase the calculated value of ν/ν_0. This might bring the computed values closer to the observed. An accurate estimate of the correction, however, would be extremely difficult to obtain.

If we calculate the radius of an orbit from the above equations, we find that it contains as a factor the square of the quantum number of the orbit, as well as other quantities. This means that the orbits having the same quantum number do not differ very much in radii, but that when the quantum number changes there is a considerable difference in radii. In the above distribution of electrons four orbits have quantum numbers of two, and four have quantum numbers of three. The radii of the two quantum orbits do not differ very much from each other, and the radii of the three quantum orbits do not differ very much from each other, but the latter are much larger than the former. It follows from this that the

distribution of electrons described by the above equations consists of two electrons in an inner orbit: then two groups of eight electrons, each, each group on the surface of a sphere, the two spheres lying fairly close together. Considerably outside of these spheres are two spherical surfaces, each containing eighteen electrons and lying fairly close together. Thus the distribution corresponds approximately with that described in the Lewis-Langmuir theory of static atoms.

Bohr[2] has recently suggested an arrangement of orbits, one outside the other, that differs slightly from the arrangement adopted in the preceding calculations. He assumes that the three quantum orbit or orbits lie between the two quantum orbits, and that for those elements which have four quantum electrons the four quantum orbits lie between the two three quantum orbits. This arrangement of electrons may be represented by the scheme

$$n_1 = 2, \quad n_2 = 4, \quad n_3 = 9, \quad n_4 = 16, \quad n_5 = 9, \quad n_6 = 4,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 3, \quad \tau_4 = 4, \quad \tau_5 = 3, \quad \tau_6 = 2.$$

In order to test this distribution of electrons I have calculated the critical absorption frequencies of the chemical elements that lie just above the inert gases in the chemical tables. The critical absorption wave-lengths have not been measured for all the inert gases themselves. In making the computations I have assumed that the distribution of the electrons is the same as that in the inert gases, and that in each case the extra electron has been taken over by the other chemical element which forms the chemical compound used in measuring the critical absorption wave-length. As a matter of fact, it makes very little difference what is done with this additional electron. Its influence on the critical absorption wave-length is, theoretically, very small. This distribution of electrons is the same as that employed above for all chemical elements up to and including argon ($N = 18$). I have, therefore, included in the computations only those chemical elements of higher atomic number than eighteen. In the case of niton ($N = 86$) the chemical element just above it is missing, and I have, therefore, calculated the critical absorption frequency for thorium. The data appear in table 3. As in tables 1 and 2 column 3 contains the data computed on the supposition that the two one quantum electrons revolve in the same orbit, whereas for the data of column 5 they are supposed to revolve in opposite directions in separate orbits, one just outside the other. It appears that the agreement between the calculated and observed values is much better for this distribution of electrons than for the preceding distributions, especially the data of column 3. Owing to the fact that the radius of the first three quantum orbits is much larger than that of the two quantum orbits inside them the correction for the mutual influence of these two and three quantum orbits becomes very small.

TABLE 3

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT, ν/ν_0		
		Calculated	Observed	Calculated
Potassium	19	262.0	266.0	243.7
Rubidium	37	1128.	1120.	1091.
Caesium	55	2649.	2648.	2591.
Thorium	90	8090.	8075.	7962.

In order to make the computations for chemical elements other than those in table 3 it appears to be necessary to make additional assumptions as to just how the elements are built up in increasing values of the atomic numbers. There is also some difficulty about the radii of the various orbits. In general, a two quantum orbit has a much smaller radius than a three quantum orbit.

The formulas of this and the preceding note contain no undetermined constants after the distribution of the electrons has been fixed; i.e., there is nothing in the equations which must be obtained from X-ray measurements themselves. The formulas are functions of numbers and of π except in the correction term for the change of mass of an electron with its velocity. The correction term is the only place where measured quantities appear. These quantities are the electron's charge e, Planck's action constant h, and the velocity of light c, and they may be regarded as having been determined by experiments other than X-ray measurements. In spite of this fact the formulas represent the observed values to within a few per cent. This is fairly close, considering the influences that have been neglected. Among the reactions that have been neglected we may mention the forces due to electrons in orbits outside the one considered, the fact that electrons inside these orbits have been supposed concentrated in the nucleus, forces due to the magnetic fields of the revolving electrons, the influence of electrons that may be out forming bonds with other chemical elements and which may not, therefore, take part in the energy changes, etc.

The fact that the various distributions considered give results that differ from each other by only a few per cent indicates that the calculation of the K critical absorption frequency is not a sensitive method of determining the *exact* distribution of the electrons. Further, other distributions than those considered may furnish more accurate values. The important point is that the distribution of electrons is what may be called the chemical distribution, and that the numbers of electrons in the orbits are related to their quantum numbers according to equation 4.

The calculation of the L and M, etc. critical absorption frequencies presents very great difficulties, for, if we suppose that an electron is removed from the second or third pair of orbits, it leaves this pair of orbits unbalanced. Just what would happen in this case is not clear, and it would require an additional assumption in order to complete the calculations. Definite general conditions of the dynamic equilibrium have not yet been found.

It may be, also, that orbits that are not circular would give better values than circular orbits. Computations of the frequencies on this basis present formidable difficulties. The fact, however, that the two quantum and three quantum orbits lie not in a plane, but in space of three dimensions may explain the appearance of three critical absorption wave-lengths in the L series, and six critical absorption wave-lengths in the M series, etc.

According to Sommerfeld's theory[3] the difference between two L absorption frequencies is due to the difference in shape of a circular and an elliptic orbit. His formula contains an undetermined constant. Professor Patterson and I have shown[4] that if we assume four electrons in the L orbit the undetermined constant is done away with, and that Sommerfeld's formula represents roughly the difference between the L_1 and L_2 absorption frequencies. It may be that a formula calculated on the basis of three dimensional orbits would give more accurate results.

I am greatly indebted to several of my assistants for carrying through many of the computations.

[1] These PROCEEDINGS, Sept., 1921, p. 260.
[2] *Nature*, March 24, 1921.
[3] *Atombau und Spektrallinien*, Chapter 5.
[4] These PROCEEDINGS, Sept., 1920, p. 517.

SEMI-COVARIANTS OF A GENERAL SYSTEM OF LINEAR HOMOGENEOUS DIFFERENTIAL EQUATIONS

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Communicated by E. J. Wilczynski, Aug. 13, 1921

It is known[1] that the most general transformation of the dependent variables which converts the system of linear homogeneous differential equations

$$y_i^{(m)} + \sum_{l=0}^{m-1} \sum_{k=1}^{n} \binom{m}{l} p_{ikl}\, y_k^{(l)} = 0, \ (i = 1, 2, \ldots, n), \qquad (A)$$

where p_{ikl} are functions of the independent variable x, into another system of the same form is given by the equations

$$y_k = \sum_{\lambda=1}^{n} \alpha_{k\lambda} \bar{y}_\lambda, \quad (k = 1, 2 \ldots, n), \tag{1}$$

where $\alpha_{k\lambda}$ are arbitrary functions of x and where the determinant Δ of the transformation does not vanish identically.

A function of the coefficients of (A) and their derivatives and of the dependent variables and their derivatives which has the same value for (A) as for any system derived from (A) by the transformation (1) is called a *semi-covariant*. If a semi-covariant does not contain the dependent variables or their derivatives, it is called a *seminvariant*. A complete system of seminvariants of system (A) has been calculated.[2] It is the purpose of this paper to obtain the additional semi-covariants necessary for a complete system of semi-covariants.

If equations (1) are solved for $\bar{y}_\lambda$, there results

$$\Delta \bar{y}_\lambda = \sum_{j=1}^{n} A_{j\lambda} y_j, \tag{2}$$

where $A_{j\lambda}$ is the algebraic minor of $\alpha_{j\lambda}$ in Δ. If the coefficients in (1) are assumed to satisfy the conditions for the transformation of (A) into the semi-canonical form,[2] the successive differentiation of (2) gives

$$\Delta \bar{y}_\lambda^{(\tau)} = \sum_{j=1}^{n} A_{j\lambda} t_{j\tau}, \quad (\tau = 1, 2, \ldots), \tag{3}$$

where

$$t_{j\tau} = t'_{j,\tau-1} + \sum_{k=1}^{n} p_{j,k,m-1} t_{k,\tau-1}, \quad t_{j0} = y_j \tag{4}$$

The most general form of (1) which leaves the semi-canonical from in the semi-canonical form is given by the equations[2]

$$y_k = \sum_{\lambda=1}^{n} a_{k\lambda} \bar{y}_\lambda, \tag{5}$$

where $a_{k\lambda}$ are arbitrary constants whose determinant D is not zero. The semi-covariants in their semi-canonical form are obtained by transforming the semi-canonical form of (A) by (5). We shall let π_{ikl} denote the coefficients of the semi-canonical form of (A) which correspond to the

coefficients p_{ikl} of (A). The effect of the transformation (5) upon $\pi^{(\tau)}_{ikl}$ is given by the equations[2]

$$D\pi^{-(\tau)}_{ikl} = \sum_{\lambda=1}^{n} \sum_{\mu=1}^{n} A_{\lambda i}\, \pi^{\tau}_{\lambda\mu l}\, a_{\mu k} \quad (l=0, 1, \ldots m-2) \qquad (6)$$

where $A_{\lambda i}$ is the algebraic minor of $a_{\lambda i}$ in D.

If we put

$$r_{il} = \sum_{j=1}^{n} \pi_{i,j,m-2}\, r_{j,l-1} \quad (i = 1, 2, \ldots n, l = 1, 2, \ldots n-1), \qquad (7)$$

where $r_{j0} = y_j$, it is easily verified that each of the sets of quantities $r_{il} (i=1, 2, \ldots\ldots, n)$ is transformed by (5) cogrediently with y_i $(i=1, 2, \ldots\ldots, n)$. Therefore, the determinant

$$R = \begin{vmatrix} y_1, & y_2 \ldots\ldots\ldots\ldots\ldots y_n \\ r_{11}, & r_{21} \ldots\ldots\ldots\ldots\ldots r_{n1} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ r_{1,n-1} & r_{2,n-1} \ldots\ldots r_{n,n-1} \end{vmatrix}$$

is a relative semi-covariant.

Again, it is evident from (6) that

$$s_i = \sum_{j=1}^{n} \pi'_{i,j,m-2}\, y_j, \quad (i=1, 2, \ldots n),$$

is a set of quantities which are transformed by (5) cogrediently with y_i $(i=1, 2, \ldots\ldots, n)$. We therefore have $n-1$ additional relative semi-covariants

$$S_i = \sum_{j=1}^{n} s_j \frac{\partial R}{\partial r_{ji}}, \quad (i=1, 2, \ldots n-1).$$

Since the coefficients in (5) are constants, each set $y_i^{(\tau)}$ $(i=1, 2, \ldots, n)$ of derivatives of y_i are transformed by (5) cogrediently with $y_i (i=1, 2, \ldots, n)$. We therefore have $mn - n$ relative semi-covariants

$$T_{l\tau} = \sum_{j=1}^{n} y_j^{(\tau)} \frac{\partial R}{\partial r_{jl}}, \quad (l=0, 1, \ldots n-1; \tau=1, 2, \ldots, m-1)$$

A comparison of (3) with the inverse of (5) and of the expressions,[2] π_{ikl}, and π'_{ikl}, in terms of the coefficients of (A), with (6) shows that the

semi-covariants R, S_i, $T_{l\tau}$ may be expressed as semi-covariants of (A) simply by replacing $y_i^{(\tau)}$ by $t_{i\tau}$, π_{ikl} by u_{ikl}, and π_{ikl} by v_{ikl}, where u_{ikl} and v_{ikl} are functions of the coefficients of (A) and their derivatives which appear in the expressions for π_{ikl} and π'_{ikl}.

If the transformation (1) and the corresponding transformations for the derivatives of y_i are made infinitesimal, and the resulting system of partial differential equations for the semi-covariants is set up, it is found that there are exactly mn relative semi-covariants which are not seminvariants. We thus have the proper number of semi-covariants, but it remains to show that they are independent.

A comparison of R and S_i with the corresponding semi-covariants[3] for the special case of (A) where $m = 2$ shows R and S_i to be independent. Again, the functional determinant of $T_{l\tau}$ with respect to $y_i^{(\tau)}$ $(i=1,2,\ldots,n)$ for each value of $\tau = 1, 2, \ldots\ldots, m-1$ shows[3] that $T_{l\tau}$ are independent, among themselves and of R, of S_i and of the seminvariants.

We have now proved the following theorem:

All semi-covariants are functions of seminvariants and of R, S_i $(i = 1\ 2, \ldots\ldots, n-1)$, $T_{l\tau}$ $(l = 0, 1, \ldots\ldots, n-1; \tau = 1, 2, \ldots\ldots m-1)$.

[1] Wilczynski, E. J., *Projective Differential Geometry of Curves and Ruled Surfaces*, Teubner, Leipzig, Chap. I.

[2] Stouffer, these PROCEEDINGS, **6**, 1920 (645–8).

[3] Stouffer, *London, Proc. Math. Soc.*, (Ser. 2), **17**, 1919 (337–52).

AN ALGORISM FOR DIFFERENTIAL INVARIANT THEORY

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1. Comprehensive as the existent theory of differential parameters is, as related to quantics

$$F = (a_0, a_1, \ldots, a_m)\ (dx_1, dx_2)^m\ (aj = a_1^j(x_1, x_2)),$$

under arbitrary functional transformations

$$x_i = x_i(y_1, y_2)\ (i = 1, 2), \tag{1}$$

developments of novelty relating to the foundations result when emphasis is placed upon the domains within which concomitants of such classes may be reducible, particularly a certain domain $R(I,T,\Delta)$ defined in part by certain irrational expressions in the derivatives of the arbitrary functions occurring in the transformations. For a given set of forms F all differential parameters previously known are functions in R of certain elementary invariants, which we designate as invariant elements, and their derivatives. The theory of invariant elements serves, therefore, to unify known theories and, for the various categories of parameters, gives a means of classification.

It leads also to systems of certain new types which I designate as orthogonal[1] and the extended orthogonal types of differential parameters, and methods of enumeration relating to these systems, both general and particular.

In the paper of which the present article is an abstract, references to the literature are only incidental to the developments but mention may be given to memoirs by Christoffel,[2] Ricci and Levi-Civita,[3] to the tract of J. E. Wright,[4] containing bibliography, and to the symbolical theory of Maschke.[5]

2. The poles of the transformations on the differentials,

$$T : dx_i = \frac{\partial x_i}{\partial y_1} dy_1 + \frac{\partial x_i}{\partial y_2} dy_2 \ (i = 1, 2),$$

are the roots of the linear forms

$$h_{\pm 1} = 2 \frac{\partial x_2}{\partial y_1} dx_1 + \left(\frac{\partial x_2}{\partial y_2} - \frac{\partial x_1}{\partial y_1} \pm \Delta \right) dx_2, \tag{2}$$

where

$$\Delta = \left[\left(\frac{\partial x_2}{\partial y_2} - \frac{\partial x_1}{\partial y_1} \right)^2 + 4 \frac{\partial x_1}{\partial y_2} \frac{\partial x_2}{\partial y_1} \right]^{\frac{1}{2}},$$

and we may place $h_{\pm 1}$ equal to exact differentials

$$\mathbf{T} : df_{+1} = h_{+1}, \ df_{-1} = h_{-1},$$

thus obtaining another transformation upon the differentials of the same degree of arbitrariness as T, since the functional determinant of f_{+1}, f_{-1} will not vanish when $\Delta \neq 0$. The quantics $df_{\pm 1}$ are relative differential covariants appertaining to a domain $R(I, T, \Delta)$ whose defining quantities are the y_1, y_2 derivatives of x_1 and x_2, and the expression Δ. The covariant relations are

$$df_{+1} = \rho_{+1}^{-1} df_{+1}, \ df_{-1} = \rho_{-1}^{-1} df_{-1}, \tag{3}$$

where

$$\rho_{\pm 1} = \frac{1}{2} \left(\frac{\partial x_1}{\partial y_1} + \frac{\partial x_2}{\partial y_2} \pm \Delta \right),$$

are the factors in $R(I, T, \Delta)$ of the determinant D of T.

3. Let

$$\partial x_1/\partial y_1 = \alpha_1, \partial x_1/\partial y_2 = \alpha_2, \partial x_2 \partial/y_1 = \beta_0, \partial x_2/\partial y_2 = \beta_1,$$
$$\partial f/\partial x_i = f_i \ (i = 1, 2),$$

and write, after Maschke, the quantic F as the m-th power of a symbolical exact differential,

$$F = (df)^m = (f_1 dx_1 + f_2 dx_2)^m = (d\varphi)^m.$$

Then when F is transformed by the inverse of T, and the result expanded, the coefficients φ_{m-2i} $(i = o, \ldots\ldots, m)$ of the terms in df_{+1}, df_{-1} are differential parameters of the domain $R(I, T, \Delta)$, forming, with $df_{\pm 1}$, a complete system in this domain. Their explicit form is

$\varphi_{m-2i}=[(\gamma_1-\Delta)f_1-2\beta_0 f_2]^{m-i}[-(\gamma_1+\Delta)f_1+2\beta_0 f_2]^i(-4\beta_0\Delta)]^{-m}(i=0,..,m)$ and the invariant relations are

$$\varphi'_{m-2i}=\rho_{+1}^{m-2i}D^i\varphi_{m-2i}\ (i=0,\ \ldots,\ m). \tag{4}$$

The functions φ_{m-2i}, df_{+1}, df_{-1} are the invariant elements.

4. By differentiation of the equations (4) relations are obtained as follows:

$$\frac{\partial^r\varphi'_{m-2i}}{\partial y_1^{r-s}\partial y_2^s}=\alpha_1^{r-s}\beta_1^s\rho_{+1}^{m-2i}D^i\frac{\partial^r\varphi_{m-2i}}{\partial x_1^{r-s}\partial x_2^s}+\delta_r^{(i)},$$

$$(r=0,\ 1,\ \ldots\ldots;\ s=0,\ \ldots\ldots,\ r;\ i=0,\ \ldots\ldots,\ m).$$

As a result, employing the transvectant symbol[5]

$$U_1V_2-U_2V_1=(U,\ V)$$

we obtain a general category of relative differential parameters,

$$\psi^{(r)}_{m-2i}=(\ldots((\varphi_{m-2i},\ Q^{(i)}),\ Q^{(i)}),\ldots,Q^{(i)})\quad(Q^{(i)}=\rho_{+1}^{m-2i}D^i),$$

the number of iterations being r, and

$$\psi^{(r)'}_{m-2i}=\rho_{+1}^{m-2i}D^{i+r}\psi^{(r)}_{m-2i};\ (i=0,\ldots,m). \tag{5}$$

We define $\psi^{(0)}_{m-2i}$ to be φ_{m-2i}.

Write

$$P_{+1}=\prod_{k=0}^{r}\psi_m^{(k)Xok}\psi_{m-2}^{(k)X_1k}\ldots\psi_{-m}^{(k)Xmk}df_{+1}^{\omega_1}df_{-1}^{\omega_1}$$

and let the conjugate product be P_{-1};

$$P_{-1}=\prod_{k=0}^{r}\psi_{-m}^{(k)Xok}\psi_{-m+2}^{(k)X_1k}\ldots\psi_m^{(k)Xmk}df_{+1}^{\omega_1}df_{-1}^{\omega_1},$$

then the parameters of the extended orthogonal type are defined to be those which can be generated in totality by forming such rational expressions in $\psi^{(k)}_{m-2i}$, $df_{\pm1}$ as simplify by multiplication into functions appertaining to the domain $R(I,T,0)$, free, that is, from the expression Δ. The essential forms from which to construct this totality are evidently $P_{+1}\pm P_{-1}$. When $r=0$ the type is called orthogonal.[1]

Finite complete systems can be derived in this theory. In fact the products P form a Hilbert system of monomials whence it follows that a complete system of concomitants of the extended orthogonal type is furnished by the finite set of irreducible solutions of the diophantine equation

$$\sum_{k=0}^{r}\sum_{l=0}^{m}(m-2l)X_{kl}-\sigma_1+\sigma_2=0. \tag{6}$$

Particular systems of the orthogonal type have been constructed by the present writer in this and previous papers for the quantics of orders one to six inclusive, the system of the sextic for example being composed of 31 parameters. For the case $r=1$, $m=2$ the system comprises eleven concomitants of the extended type as follows:

$$\varphi_0,\ \psi_0^{(1)},\ n=\varphi_2\varphi_{-2},\ o=(\varphi_2,\ \rho_{+1}^2)\ (\varphi_{-2},\ \rho_{-1}^2),$$
$$p_{+1}=\varphi_2(\varphi_{-2},\ \rho_{-1}^2)\ \pm\ \varphi_{-2}(\varphi_2,\ \rho^2{}_{+1}),$$

$$q_{\pm 1} = (\varphi_2, \rho^2_{+1})df^2_{+1} \doteq (\varphi_{-2}, \rho^2_{-1})df^2_{-1},$$
$$r_{\pm 1} = \varphi_2 df^2_{+1} \doteq \varphi_{-2} df^2_{-1}, s = df_{+1} df_{-1}.$$

5. A paper giving the above and other developments in particular is to appear in the September (1921) number of the *Annals of Mathematics*. An article relating to the rôle of invariant elements[6] in algebraic orthogonal and boolean invariant theory appeared in the *Transactions* of the American Mathematical Society, vol. 20 (1919), and a paper containing like theory for invariants of relativity and modular invariants appeared in the same *Transactions* for the year 1920. Further researches are in progress.

[1] Elliott, *Proc. London Math. Soc.*, **33** (1901).
[2] Christoffel, *Crelle, J. Math.*, **70** (1869).
[3] Ricci and Levi-Civita, *Math. Ann.*, **54** (1901).
[4] J. E. Wright, *Invariants of Quadratic Differential Forms*, Cambridge tracts (1908).
[5] Maschke, *Trans. Amer. Math. Soc.*, **1** (1900); **4** (1903).
[6] O. E. Glenn, *Ann. Math.*, **20** (1918).

THE EFFECT OF TEMPERATURE AND OF THE CONCENTRATION OF HYDROGEN IONS UPON THE RATE OF DESTRUCTION OF ANTISCORBUTIC VITAMIN (VITAMIN C)

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In these experiments the vitamin was determined by means of feeding experiments with guineapigs according to the general method made familiar by Hess' recent monograph.[1] Cohen and Mendel,[2] Givens and McCluggage,[3] and the workers at the Lister Institute[4] among other investigators of the antiscorbutic vitamin, have emphasized the importance of basal diets which shall supply all other nutritive requirements and yet furnish none of the vitamin in question or only negligible traces of it. Further investigation of this point led the present writers to adopt the following as an improvement upon the diets previously proposed.

Basal Ration Used.—Ground whole oats were mixed with skimmed milk powder which had been heated sufficiently to ensure destruction of such antiscorbutic vitamin as it might contain without so changing the flavor as to cause it to be refused by the experimental animals. The heat treatment necessary to ensure complete destruction of vitamin C in the skimmed milk powder should be determined by each investigator for his own material and technique of heating. In our experiments two hours' heating

at 110° C. in shallow trays freely exposed to air was found sufficient. To the mixture of oats and skimmed milk powder were added pure fresh butterfat and sodium chloride. The proportions adopted were:

Ground whole oats	59 per cent
Heated skimmed milk powder	30 per cent
Butterfat	10 per cent
Sodium chloride	1 per cent

By using heated skimmed milk and fresh butterfat instead of heated whole milk, the absence of antiscorbutic vitamin is equally well ensured and the palatability of the diet and its fat-soluble vitamin content are improved. This diet supports excellent growth up to the time of the onset of scurvy.

Experimental Animals.—Our experience with about 200 experimental animals indicates that young guineapigs from six to eight weeks old and weighing 300 to 350 grams are best used for studies of vitamin C. Placed upon the above ration at this age and size they usually eat about 18 to 20 grams per day and continue to grow for about 15 days, then lose weight rapidly and die of scurvy in from 26 to 34 days after being confined to the diet. If much older, the animals are somewhat less susceptible; if much younger, the results are less regular.

Symptoms, Survival Period, and Autopsy Findings.—The first symptoms appear after about 12 days on the basal diet. In our cases on the above basal diet only, the survival periods were, respectively, 33, 26, 27, 28, 34, 28, 27, 34, 26, 29, 32, 32, 32, 31, 34 days. The nature of the symptoms and autopsy findings agreed so closely with the descriptions of Cohen and Mendel and of Hess as not to require further discussion here. At autopsy the findings which proved most significant were: looseness of teeth, fragility of bones, enlargements and hemorrhages of joints and of rib junctions. When the animal receives some antiscorbutic vitamin but not enough for protection from scurvy, life is prolonged, but to a rather uncertain extent, and some of the symptoms and autopsy findings may become even more severe than in the animals that receive no antiscorbutic and die more quickly.

Quantitative Rating.—From what has just been said it necessarily follows that exclusive dependence upon either the survival period or any one set of symptoms or autopsy findings might easily prove misleading. All of these are, therefore, considered in each case. This was done with several series of animals, some receiving the basal ration only, and others measured amounts of filtered canned tomato juice up to the amount which gave complete protection from scurvy. By comparison with the standard protocols thus established, for data of which reference must be made to the fuller account of the work to be published elsewhere, it becomes possible to form a quantitative estimate of the degree of protection (if any)

which the diet, alone or with such antiscorbutic addenda as have been introduced, has afforded the animal.

Effect of Heating in Acid Solution.—In the case of tomato juice of natural acidity, pH = 4.3, it was found that boiling for one hour destroyed practically 50%, and for four hours destroyed practically 68% of the antiscorbutic vitamin present. The time curve of the destructive process is, therefore, much flatter than that of a unimolecular reaction or of a reaction proceeding according to the square root rule of Schütz. Similar flattening of the time curves of the destruction of the vitamin were found also in experiments in which the tomato juice was heated at temperatures lower than boiling, viz., at 60° and at 80°. Comparisons of the data obtained at 60°, 80° and 100° show relatively low temperature coefficients: Q_{10} (60°–80°) = 1.23; Q_{10} (80°–100°) = 1.12.

Effect of Reduced Concentration of Hydrogen Ions.—In experiments in which the natural acidity of the standard tomato juice was first neutralized in whole or in part, the juice then boiled for one hour and immediately cooled and reacidified, it was found that at pH 5.1 to 4.9 (natural acidity less than half neutralized) the destruction during one hour's boiling was increased to 58%. Neutralization of a larger proportion of the natural acidity increased the rate of destruction of the vitamin. When alkali was added to an initial pH of 11, which fell to about 9 during the hour of heating, the destruction found by feeding of the juice thus treated but immediately cooled and reacidified, was about 65%.

In all of these experiments the heating was performed in cotton-stoppered, narrow-necked flasks from which air was probably very largely displaced by water vapor early in the heating. When the experiments upon heating at 100° were repeated with oxygen bubbling through the solution the destruction of the vitamin was much more rapid.

Heating at 100° for one hour at pH = 11 to 9 as described above followed by standing for one to five days in stoppered but only partially filled bottles in a refrigerator at 10° C. at an alkalinity of only pH = 9 was found to destroy 90 to 95% of the antiscorbutic vitamin, as compared wth 65 per cent when the solution was re-acidified after heating. This confirms the observations of Harden and of Hess upon the susceptibility of this vitamin to alkalinity even at low temperatures.

Thus while the great instability of the antiscorbutic vitamin makes it an unpromising material for attempts at actual isolation, the development of methods for its quantitative measurement makes possible the study of its chemical behavior.

[1] Hess, A. F., *Scurvy Past and Present*, Philadelphia, 1920.

[2] Cohen, B. and Mendel, L. B., *J. Biol. Chem.*, **35**, 1918 (425).

[3] Givens, M. A. and McCluggage, H. B., *Ibid.*, **37**, 1919 (255).

[4] Chick, H., Hume, E. M., Delf, E. M. and others; A series of papers in *Biochem. J.*, 1918, et seq.